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LIQUID CRYSTALLINE POLYMERS BY CATIONIC POLYMERIZATION

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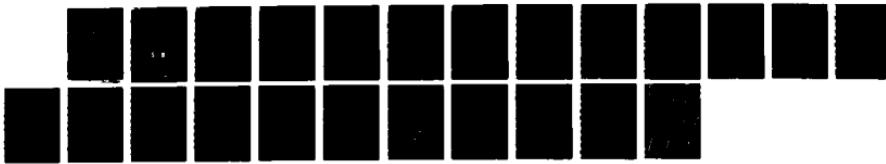
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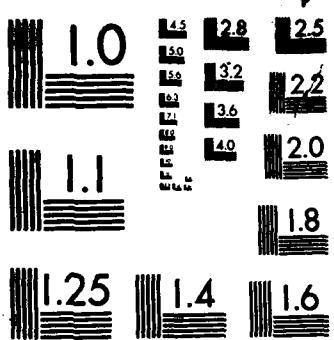
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Liquid Crystalline Polymers by Cationic Polymerization

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ABSTRACT

The synthesis of liquid crystalline polymers and oligomers containing calamitic and disc-like mesogens by cationic polymerization and oligomerization is reviewed. Examples from ring-opening, carbocationic, and radical-cation polymerizations and oligomerizations are discussed.

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LIQUID CRYSTALLINE POLYMERS BY CATIONIC POLYMERIZATION

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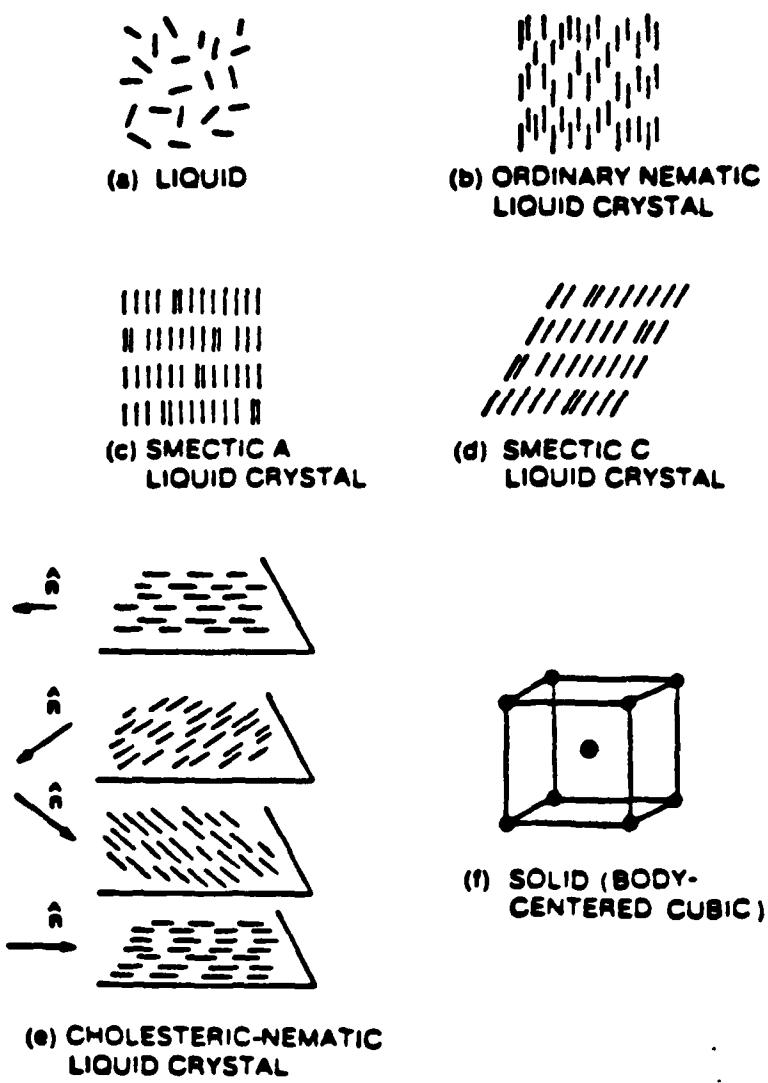
Abstract - The synthesis of liquid crystalline polymers and oligomers containing calamitic and disc-like mesogens by cationic polymerization and oligomerization is reviewed. Examples from ring-opening, carbocationic, and radical-cation polymerizations and oligomerizations are discussed.

INTRODUCTION

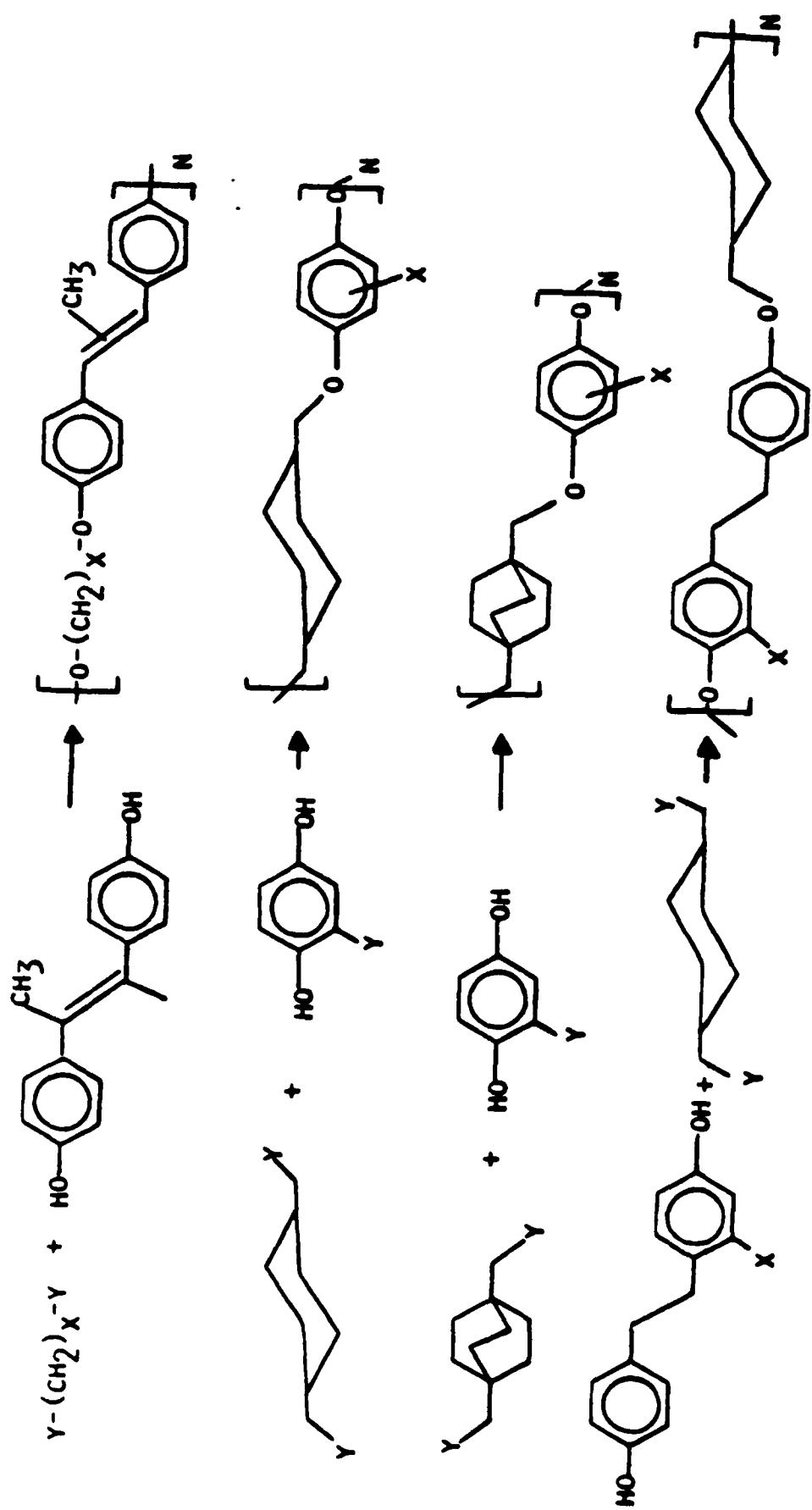
This paper will discuss briefly the role of cationic polymerization and oligomerization in the synthesis of liquid crystalline polymers and oligomers based on both calamitic or rod-like, and disc-like mesogens. The philosophy behind presenting such a review in front of the cationic polymerization community is as follows. This community has reached scientific maturity, and therefore, at the present time, more and more researchers are transplanting themselves from the field of pure physical chemistry of cationic polymerization into the field of macromolecular engineering which enables them to design and tailor novel macromolecular architectures. A very young field of organic polymer chemistry which requires this kind of expertise is that of liquid crystalline polymers. Unfortunately, very few scientists active in the area of cationic polymerization are aware of the potential and the need of their chemistry in the liquid crystal field, and at the same time, very few liquid crystal scientists are familiar with the synthetic capabilities of cationic polymerization. Therefore, in an attempt to bridge the gap between these two communities, I have decided to present such a brief review in front of the cationic polymerization community hoping that the proceedings of this meeting will then be followed with some interest by the liquid crystal community. It is the final goal of this paper to demonstrate that although at the first site there seem to be no relationship between these two areas, it could be that in fact the first examples of thermotropic main chain liquid crystalline polymers were synthesized by cationic ring-opening polymerization. At the same time, it will be demonstrated that due to the lack of communication between these two areas, some of the simplest and best controlled cationic oligomerization reactions which are frequently used by liquid crystal synthetic chemists are not quite familiar to the cationic polymerization community. This discussion will consider liquid crystal polymers (LCP) and oligomers containing calamitic or rod-like and disc-like mesogens,

LIQUID CRYSTAL POLYMERS CONTAINING CALAMITIC MESOGENS

Liquid crystals of rod-like or calamitic molecules were discovered by Reinitzer in 1888 (1) and the simplest classification of their mesomorphic behavior is outlined in Scheme 1 and compared with the molecular arrangement in isotropic liquids and crystalline solids. Systematic investigations on thermotropic liquid crystalline polymers started in 1975 when de Gennes predicted that the insertion of calamitic mesogens in the main chain of a polymer backbone or as side-groups to a polymer backbone should lead to thermotropic liquid crystalline polymers (2). Although unpublished or patented research on thermotropic main chain and side-chain LCP was performed in the early 1970's, the first published paper on thermotropic polyesters was almost simultaneous (3) with de Gennes' prediction. Systematic



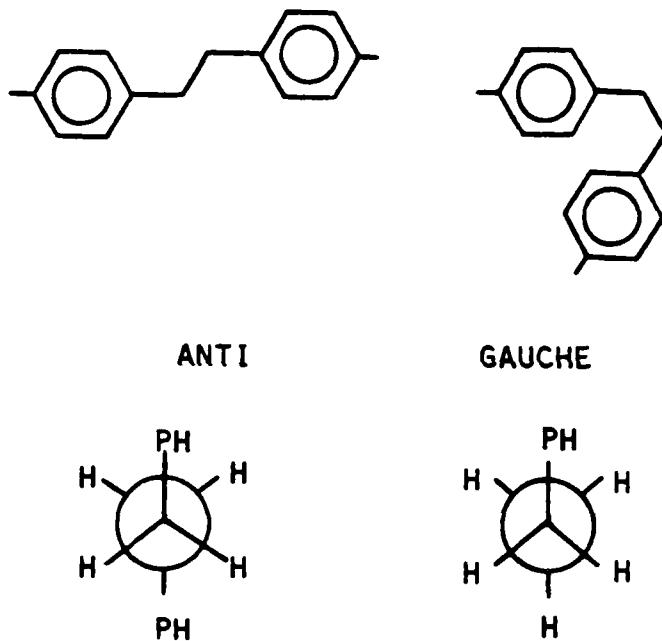
Scheme 1. A schematic representation of the molecular arrangement (a) in the isotropic liquid ; (b) in the nematic liquid crystal; (c) in the smectic A liquid crystal; (d) in the smectic C liquid crystal; (e) in cholesteric liquid crystal; (f) in crystalline solids (a dot represents a molecule)



Scheme 2. Synthesis of LC polyethers by phase transfer catalyzed polyetherification

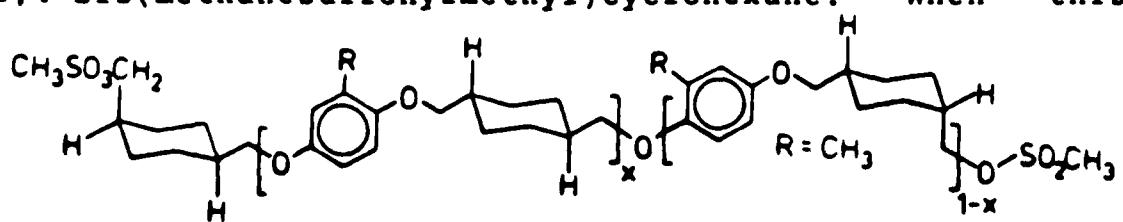
investigations on side-chain thermotropic LCP began only after Ringsdorf et al have advanced the spacer concept to decouple the motion of the side-chains from that of the main chain (4, 5). This field was extensively reviewed (6) and more recently, LCP containing a large variety of structural principles became available mostly from Ringsdorf's group (7).

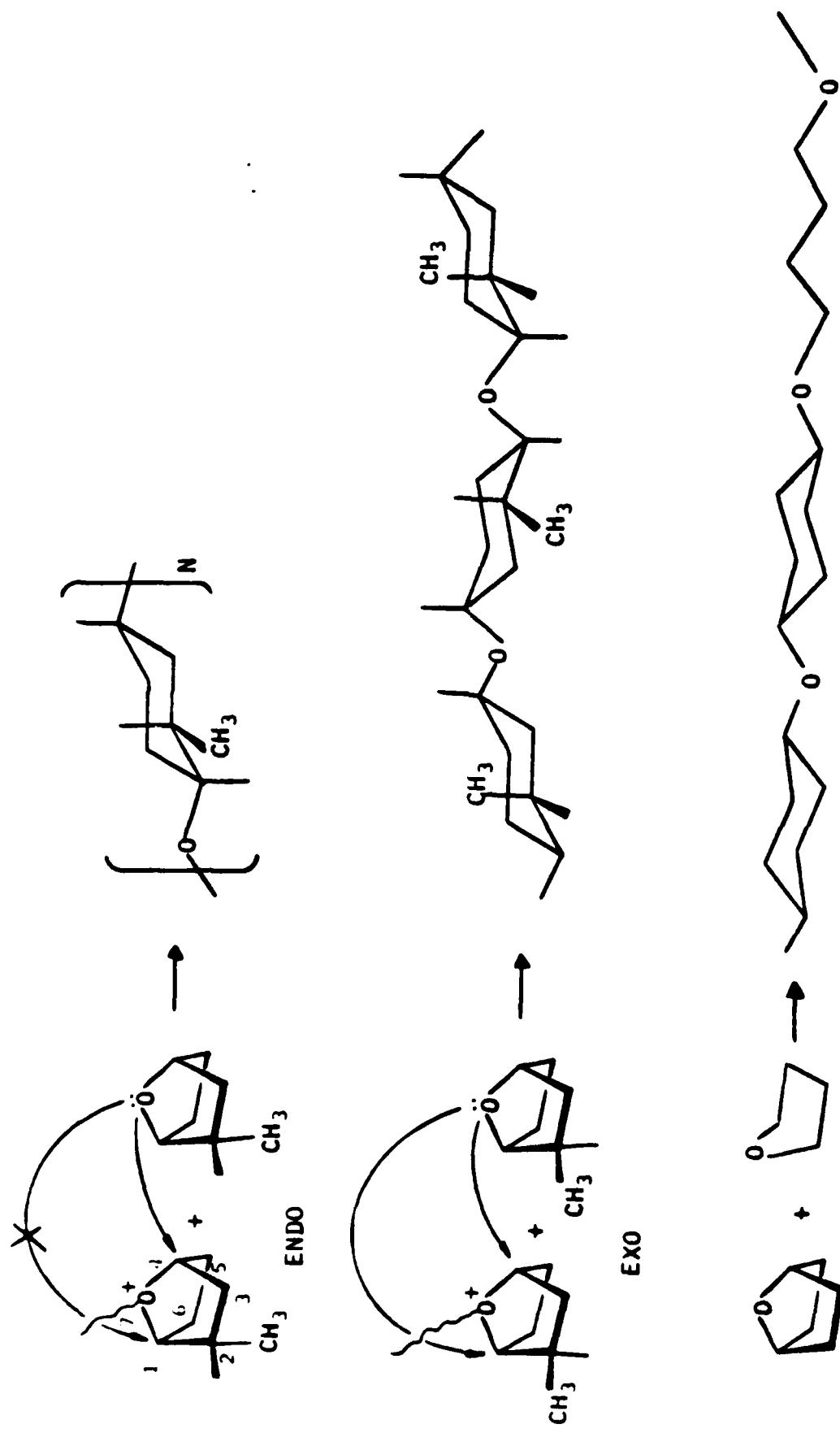
The first liquid crystalline polyethers were reported in 1984 from our laboratory being prepared by the phase transfer catalyzed polyetherification of mesogenic bisphenols with dielectrophilic spacers (8). Some of the polymer structures exhibiting liquid crystalline properties are outlined in Scheme 2. As we can observe from Scheme 2, with the exception of the polymers based on 4,4'-dihydroxy- α -methylstilbene, the other do not contain rod-like mesogenic units. In spite of this, all of them exhibit mesomorphic properties. Their mesomorphic character is due to the fact that flexible



Scheme 3. Conformational isomerism of diphenyl ethane, benzyl ether and methylene ether units

diphenyl ethane, benzyl ether and methylene ether units, exhibit two stable i.e., anti and gauche conformational isomers as shown in Scheme 3. The anti conformer has an extended conformation similar to a rigid rod-like ester unit, and therefore exhibits liquid crystallinity. The overall behavior of these polymers is controlled by the dynamic equilibrium between the anti and gauche isomers and therefore it can be assumed that they have a dynamic composition. The only polyether of potential interest to the cationic community is the one based on methylhydroquinone and trans and cis-1,4-bis(methanesulfonylmethyl)cyclohexane. When this



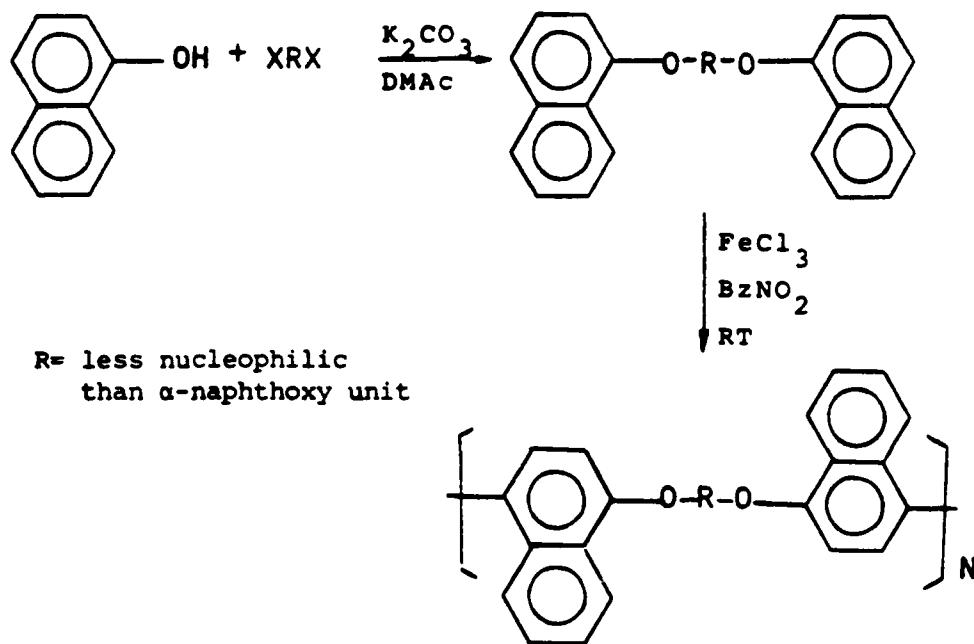


Scheme 4. Synthesis of LC polyethers by cationic ring-opening polymerization of bridged bicyclic ethers

polymer contains mesylate end groups, it is thermally depolymerizable. At 180°C methanesulfonic acid forms from the polymer chain ends, and it induces a very quick cationic depolymerization. It just happens that at 180°C this polymer is in its nematic mesophase and therefore this seems to be the first example of cationic depolymerization which takes place in the LC mesophase. This polymer has potential applications in the area of photoresists. Some recent papers from our laboratory are reviewing this work and they will not be discussed here (9-12). The major conclusion we wanted to obtain by summarizing these very few results is that the synthesis of thermotropic LC polyethers based on calamitic-like mesogens, does not necessarily require rigid rod-like mesogenic units. They can be also obtained from pro-mesogenic flexible molecules exhibiting conformational isomerism, when at least one of the stable conformational isomers can give rise to an extended conformation.

The synthesis of thermotropic LC polyethers by cationic ring-opening polymerization is outlined in Scheme 4. Contrary to the general consent, LC polyethers were in fact available almost twenty years before LC polyesters were synthesized. Nevertheless, it took exactly thirty years to realize that the polymers from Scheme 4 exhibit liquid crystallinity (13, 14). Both the cationic homopolymerization of the endo and exo-2-methyl-7-oxabicyclo[2.2.1]heptane and 7-oxabicyclo[2.2.1]heptane, as well as the copolymerization of the last one with tetrahydrofuran and/or ethylene oxide were first reported at the ACS meeting from Dallas in April 1956 (15) and published in 1960 (16). Subsequently, the cationic polymerization of these and other atom-bridged bicyclic ethers, was extensively investigated by several research groups (17), and the study of their polymerization stereochemistry became the classic experiment demonstrating the S_N^2 mechanism of cationic ring opening polymerization of cyclic ethers (18). This experiment is also important in understanding the role of constitutional isomerism on phase transitions, and it will be briefly described here. According to the S_N^2 propagation mechanism (Scheme 4), one of the two α -carbon atoms (C_1 and C_4) of the cyclic oxonium should undergo a Walden inversion to produce the polyether in which the two ether groups at C_1 and C_4 of a cyclohexane ring are trans to each other. As illustrated by Scheme 4, when the 2-methyl group is in the endo position, the attack on C_1 is sterically prohibited and the resulted polyether has all the methyl groups in equatorial positions. In the case of the exo isomer, both the attack at C_1 and C_4 are allowed, and the resulting polyether is a copolymer containing axial and equatorial methyl groups. It is essential to mention that the constitutional isomeric copolymer obtained from the exo isomer has melting transitions which are consistently lower with about 75-100°C than of the corresponding polymer obtained from the endo monomer i.e., $T_m^{(endo)} = 257^\circ\text{C}$, $T_m^{(exo)} = 188^\circ\text{C}$, while the melting point of the corresponding unsubstituted polymer is 450°C. This constitutional isomerism affects in a similar way the polymer solubility i.e., while poly(exo) dissolves only in m-cresol, poly(exo) is soluble in conventional solvents like chloroform and tetrahydrofuran.

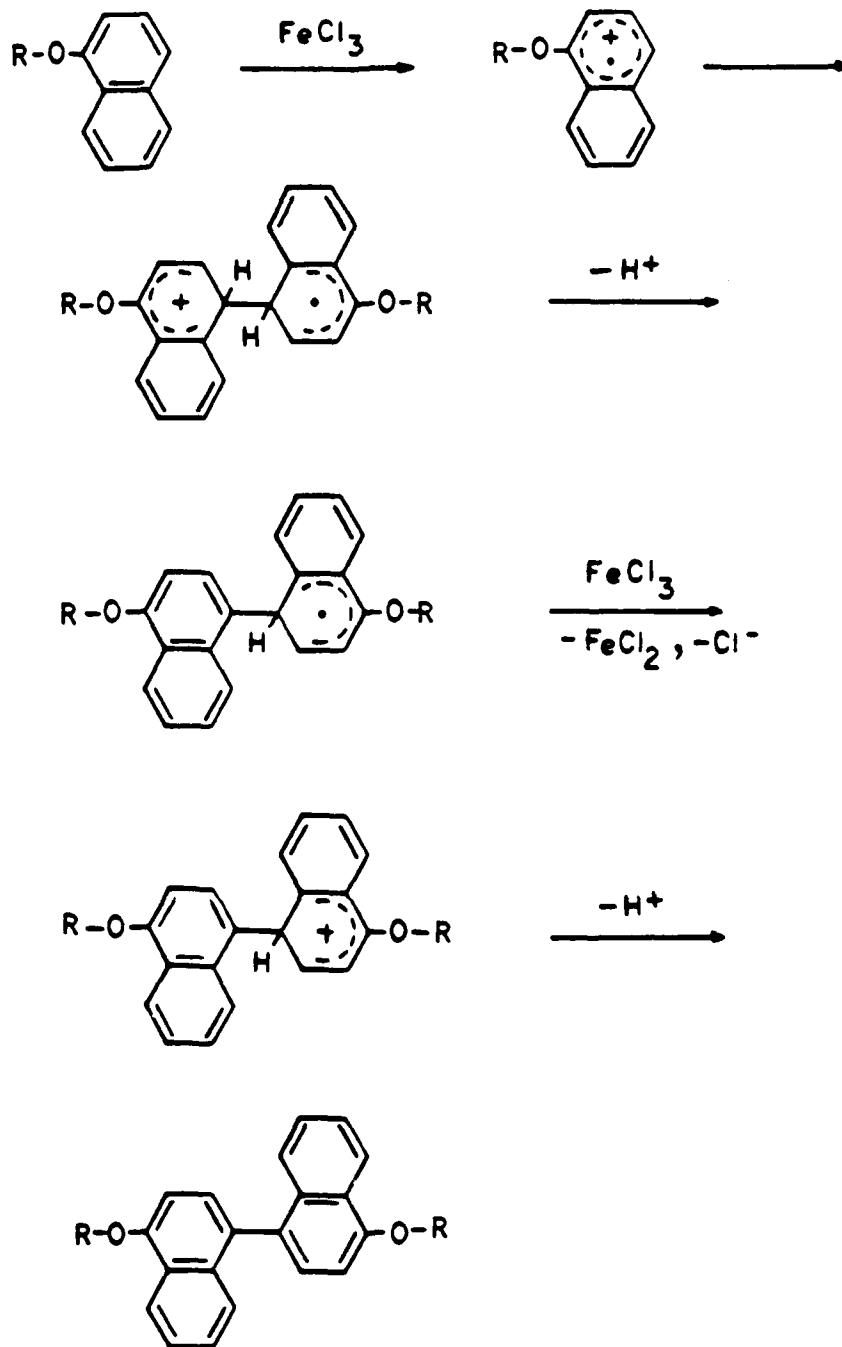
It is certain from this short discussion that cationic ring-opening polymerization can provide additional examples of LCP which are not available by any other synthetic method.



Scheme 5. Synthesis of poly(1,1'-dinaphthylether)s by Scholl reaction

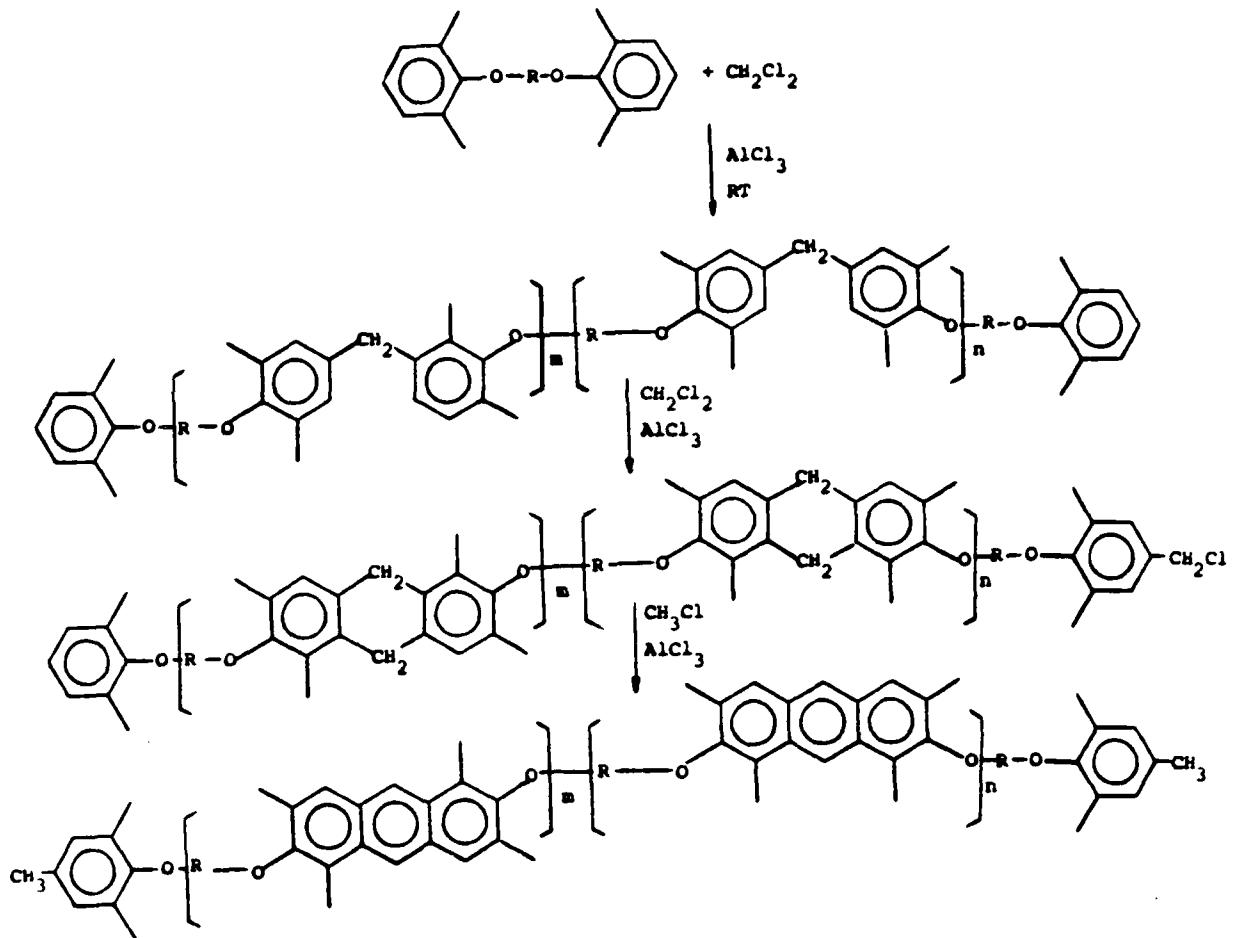
Scheme 5 outlines a novel polymerization reaction which proceeds through a cation-radical mechanism as shown in Scheme 6. This reaction is based on the well known Scholl reaction (19-22), and we have recently expanded this synthetic method to the preparation of aromatic polyethers (23). With a proper selection of the R group from Scheme 5, this polymerization reaction is expected to lead to a very simple and convenient method for the synthesis of LC polyethers.

Scheme 7 outlines a novel and unique synthetic method recently developed in our laboratory for the preparation of aromatic polyethers containing 2,6(7)-dihydroxy[1,3,5(6),7(8)-tetramethylanthracene] units (24). This reaction is based on the electrophilic copolymerization of 4,4'-bis(2,6-dimethylphenoxy) derivatives containing nonnucleophilic R groups, with methylene chloride used both as comonomer and as solvent. The polymerization mechanism is outlined in Scheme 7. It proceeds by formation of a substituted benzyl chloride derivative that represents a better electrophile than methylene chloride, and therefore, reacts very quickly with another 4,4'-bis(2,6-dimethylphenoxy) derivative to propagate the polymerization through diphenylmethane units. The diphenylmethane units react further with methylene chloride by an intrachain electrophilic substitution to form dihydroanthrylene structural units. The tetramethylsubstituted diphenylmethane derivatives provide enough steric hindrance to avoid the electrophilic substitution by the benzyl chloride derivatives of the vicinal chains. Therefore, only the intrachain electrophilic substitution reaction is allowed. The dihydroanthrylene structural units are dehydrogenated and transformed into the corresponding anthrylene units. This reaction requires a hydride abstraction in the first step, followed by a proton abstraction. The aromatization reaction is catalyzed both by

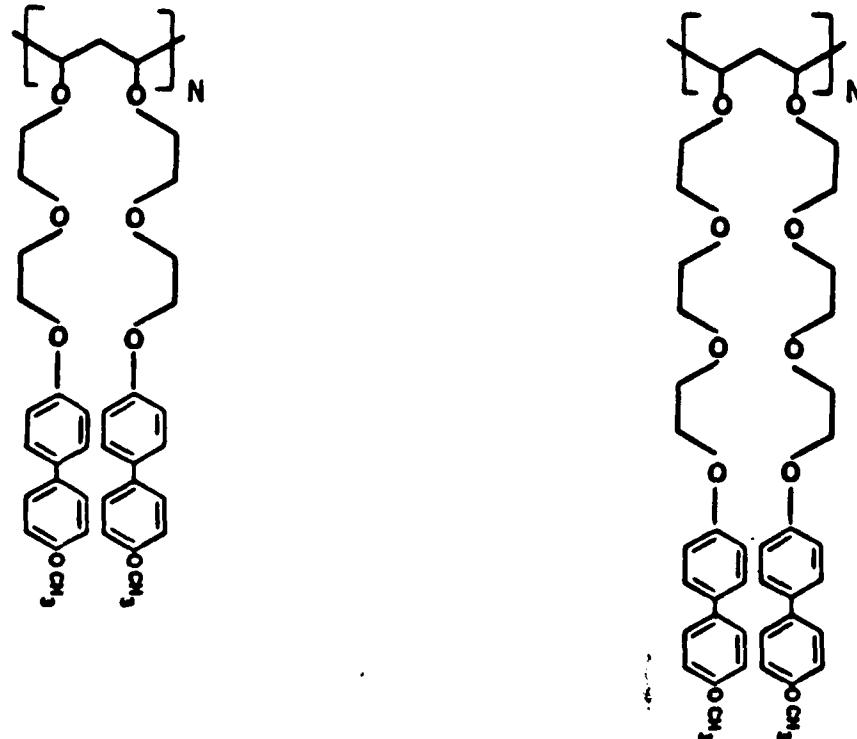


Scheme 6. The radical-cation mechanism of Scholl reaction

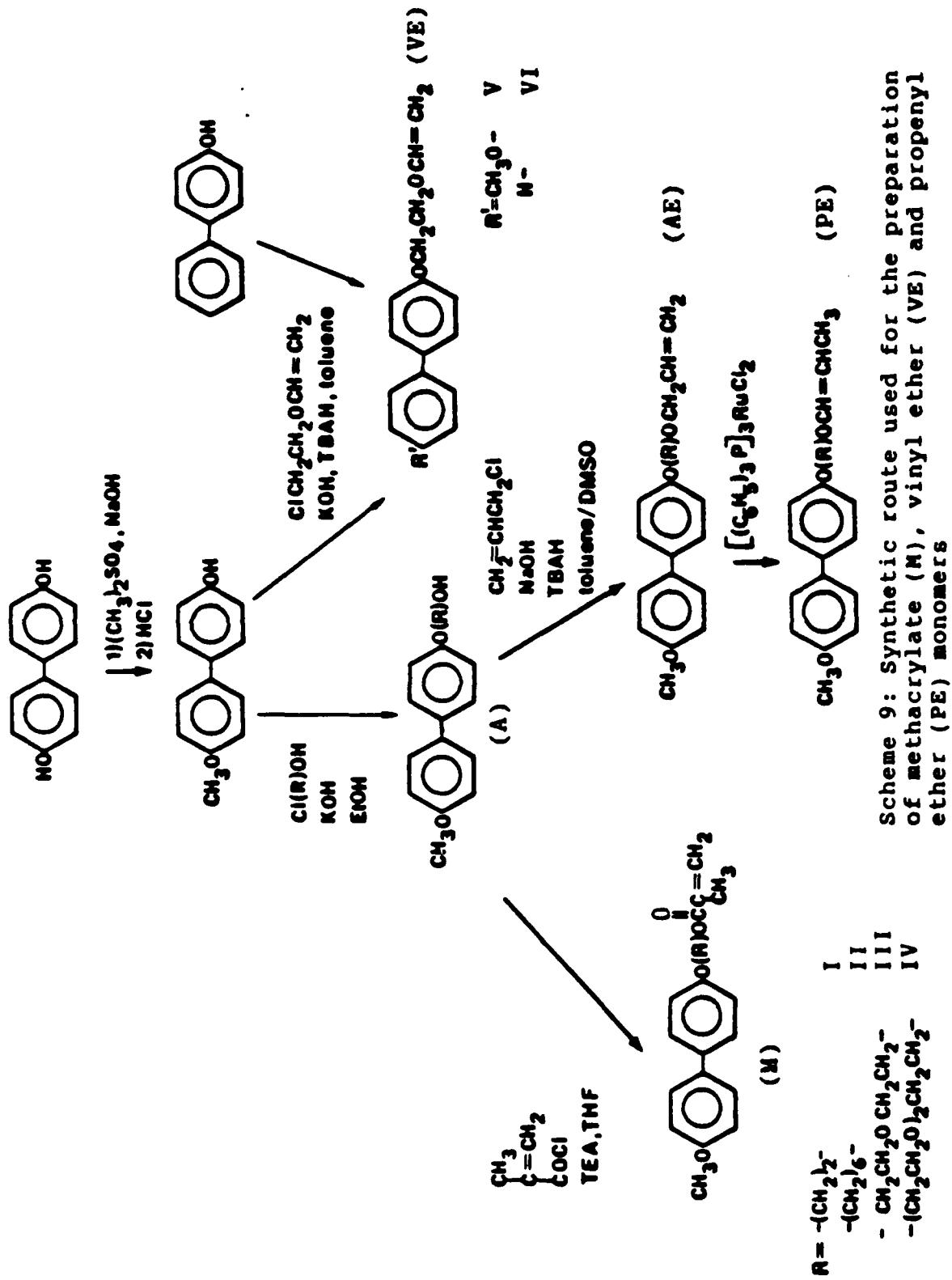
the Lewis acid and by the benzylic carbocations. Hydride transfer to benzylic carbonium ions leads to methyl groups that can be either terminal or pendant. A detailed structural characterization of this polymerization is described elsewhere (24). This novel polymerization reaction is currently investigated for the synthesis of thermotropic main chain LCP containing both calamitic and disc-like mesogens. The first examples of side-chain LCP synthesized by cationic polymerization were reported in 1986 from our laboratory (25). The idea behind this work was to prepare liquid crystalline pseudo-crown-ether polymers as outlined in Scheme 8. Scheme 9



Scheme 7. Synthesis of anthracene containing polyethers



Scheme 8. Crown ether-like side-chain liquid crystalline polyethers



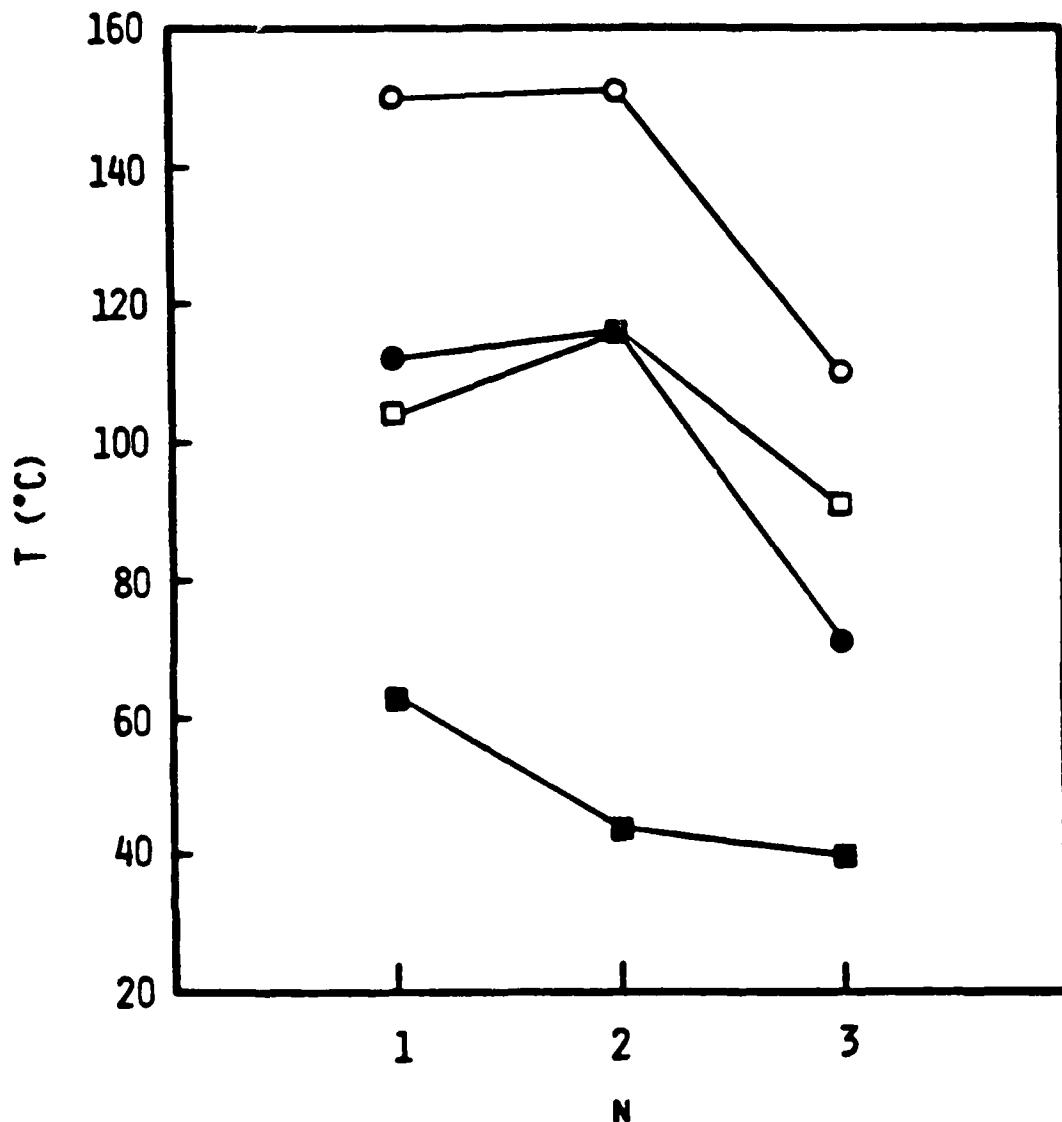
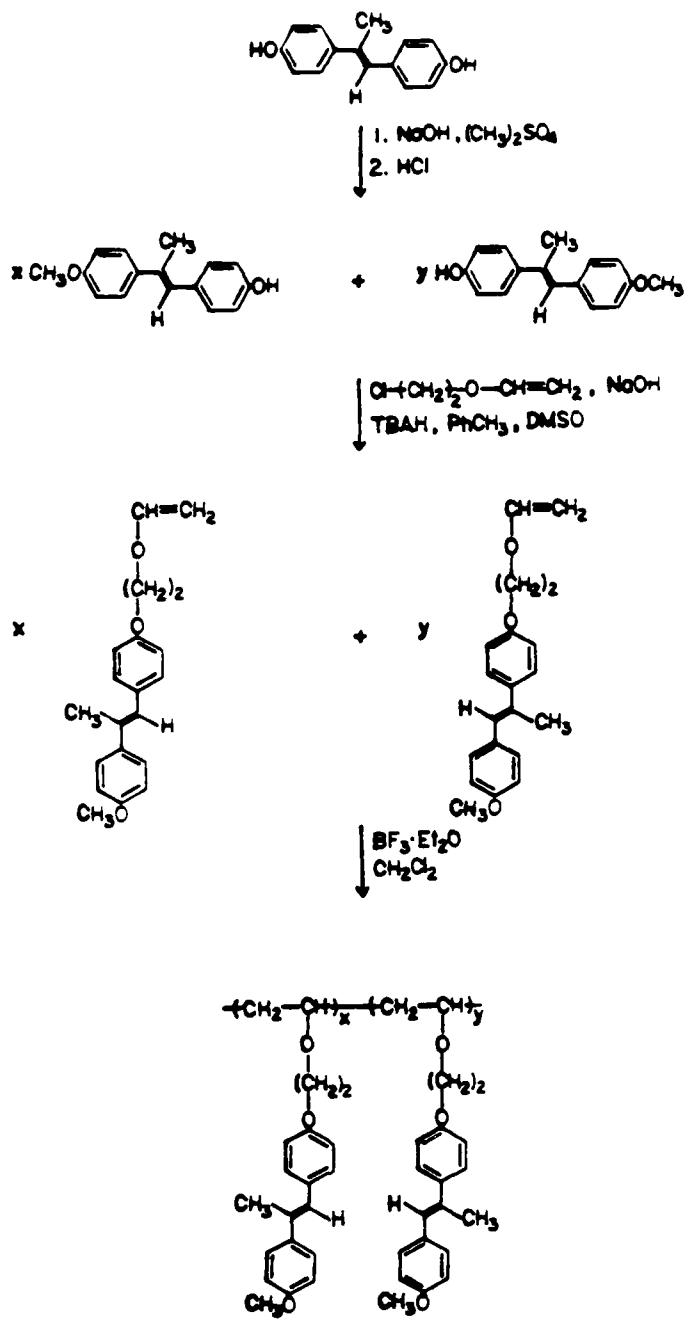


Figure 1. The dependence between the number of oligooxyethylene units in the polymer spacer (N) and the thermal transition temperature of the corresponding polymers: $\blacksquare - T_g$ (PE); $\bullet - T_g$ (M); $\square - T_i$ (PE); $\circ - T_i$ (M).

outlines the synthesis of a variety of vinyl ethers, propenyl ethers and methacrylates. Vinyl ethers and propenyl ethers were polymerized by cationic mechanism, while methacrylates were polymerized with radical initiators. The thermal behavior of all these polymers is summarized in Figure 1. In all cases the thermal stability of the mesophase is broader for the case of poly(vinyl and propenyl ether)s when compared to the behavior of the corresponding polymethacrylates. These results have demonstrated that for the same spacer, mesogenic unit, and polymer backbone, the interconnecting group between spacer and backbone plays an unexpectedly important role in decoupling the motion of the side-groups from that of the main chain.

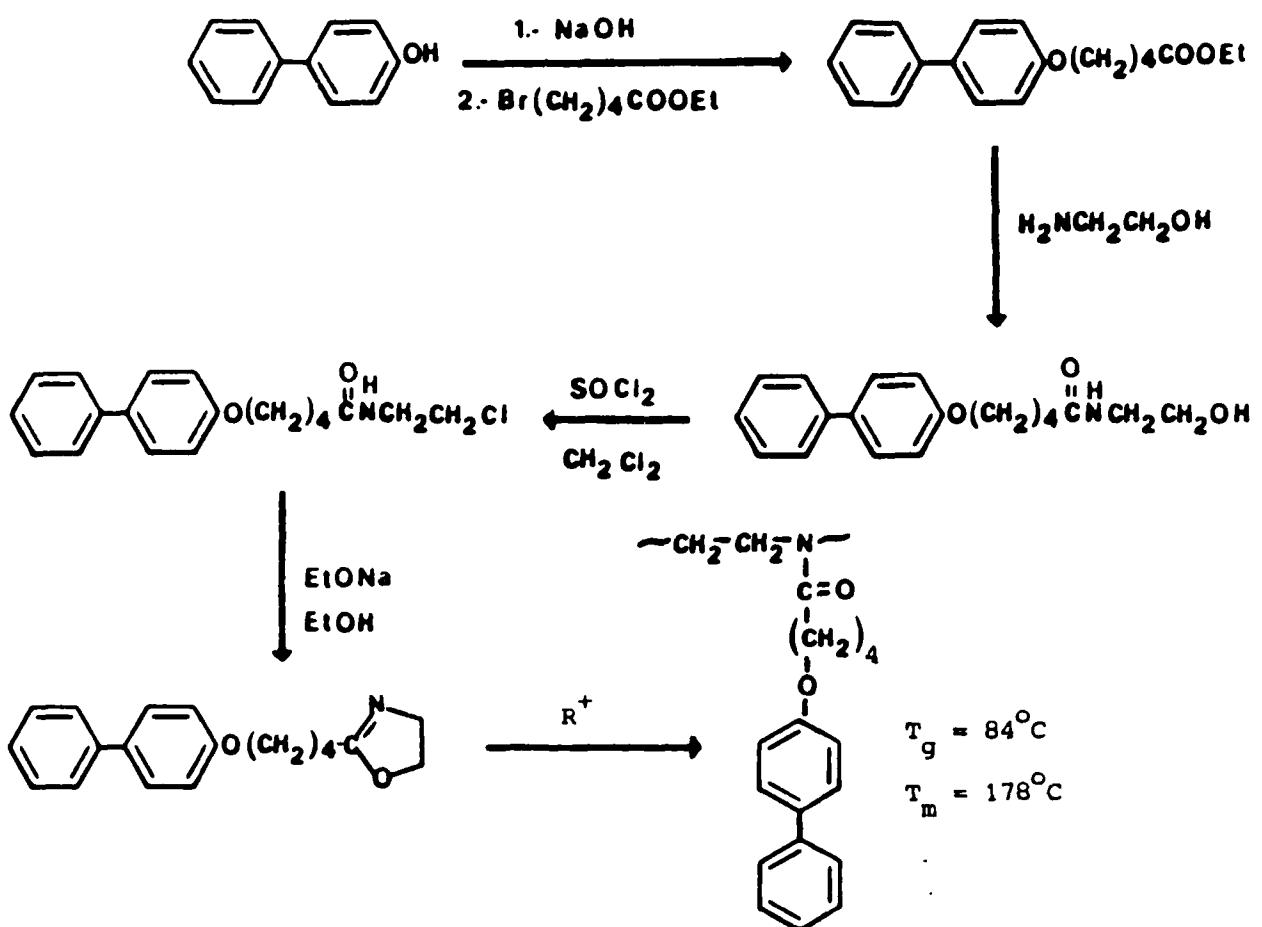
Scheme 10 describes an other experiment which was recently performed with liquid crystalline vinyl ethers (26). It consists in the cationic copolymerization of monomer pairs of



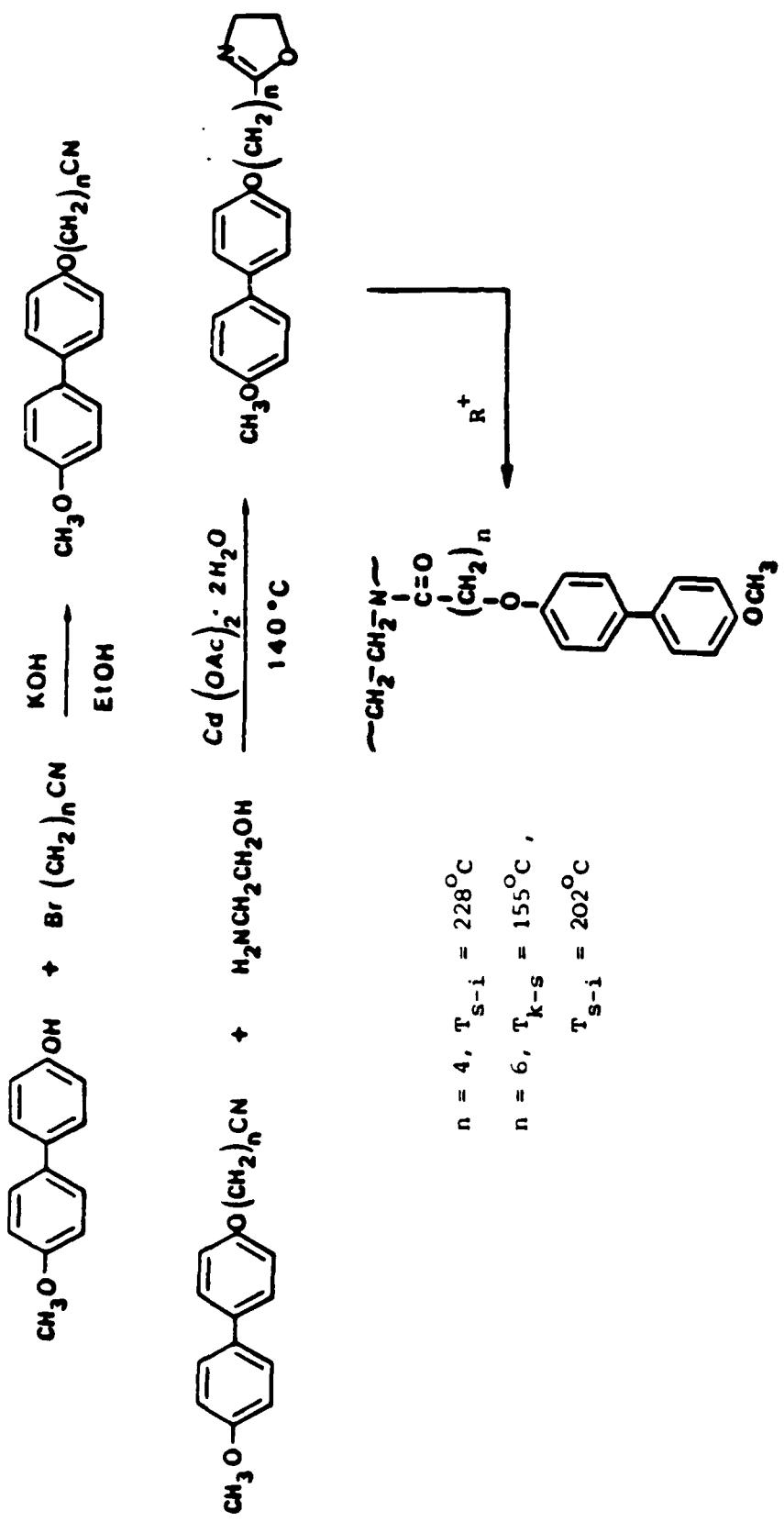
Scheme 10. Synthesis of copoly(vinyl ether)s containing 4(4')-methoxy-4'(4)-hydroxy- α -methylstilbene constitutional isomers as side groups

ethoxy vinyl ethers containing 4-methoxy-4'-hydroxy- α -methylstilbene and 4-hydroxy-4'-methoxy- α -methylstilbene constitutional isomers as side-groups. Cationic copolymerization of various ratios between the two constitutional isomeric monomers led to a mixture of two copolymers which were identified by gel permeation chromatography and were separated by fractional precipitation. One of the two copolymers exhibits a nematic mesophase, while the other exhibits two smectic mesophases. It has been speculated that these copolymerizations led to two copolymers, because two independent propagating species are

responsible for the propagation reaction when $\text{BF}_3 \cdot \text{Et}_2\text{O}$ is used as initiator. Therefore, they lead to two sets of rate constants of propagation, which in turn are providing two sets of reactivity ratios for the same monomer pair, and consequently, a single copolymerization experiment can provide two copolymers with different compositions. In this particular case, one composition gives a nematic copolymer while the other composition gives a smectic copolymer. Since smectics are not miscible with nematics, they could be easily separated by fractionation. It is interesting to mention, that the copolymethacrylates and copolyacrylates containing the same mesogenic units and two methylenic groups in the flexible spacer give only nematic mesophases independent of their composition (26). The formation of smectic polymers by replacing the ester interconnecting group by an ether one, supports the previous statement (25) that the degree of decoupling of the side-groups from the main chain is not dependent on the spacer length only, but also on the nature of the backbone-spacer interconnecting group, and on the nature of the polymer backbone (12, 26).



Scheme 11. Synthesis of poly(N-acylethyleneimine) containing 4-biphenol based side-groups

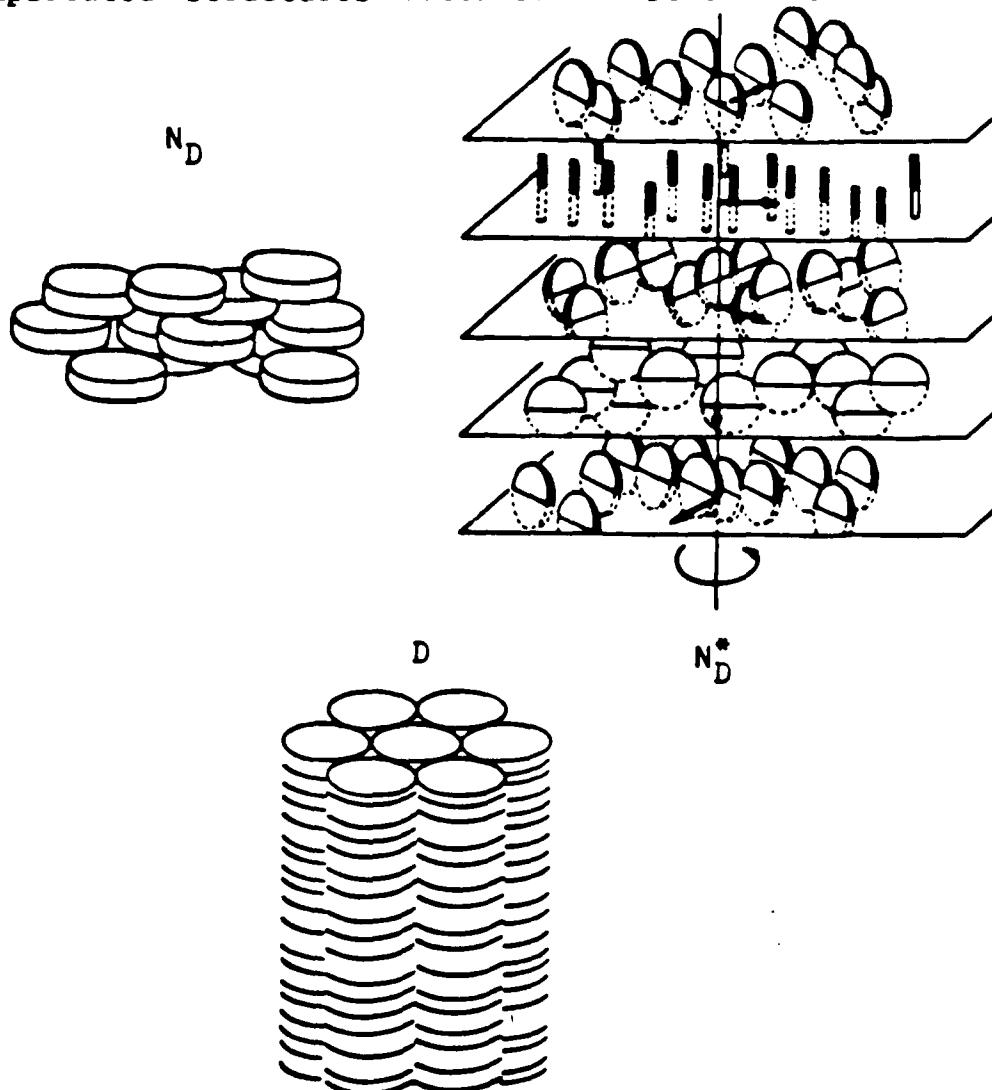


Scheme 12. Synthesis of poly(N-acyleneimine)s containing 4-methoxy-4'-hydroxybiphenyl based side-groups

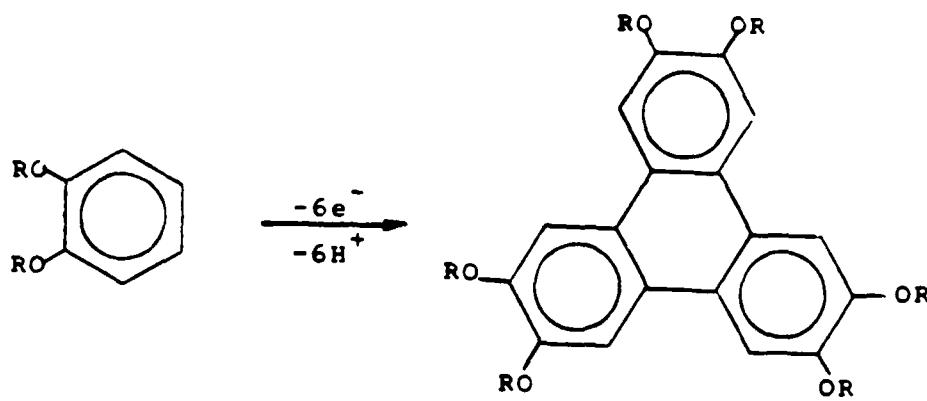
Schemes 11 and 12 outline the preparation of the first examples of liquid crystalline poly(N-acylethyleneimine)s by cationic ring opening polymerization of the corresponding cyclic imino ethers (27). The polymer containing 4-hydroxybiphenyl based side-groups is as expected only crystalline (Scheme 11). The polymers containing 4-methoxy-4'-hydroxybiphenyl side-groups are all liquid crystalline, but because of their highly rigid backbone they crystallize and provide polymers soluble only at high temperatures, and consequently no living polymerization or at least good control over their molecular weights could be obtained (27).

DISC-LIKE LIQUID CRYSTALS

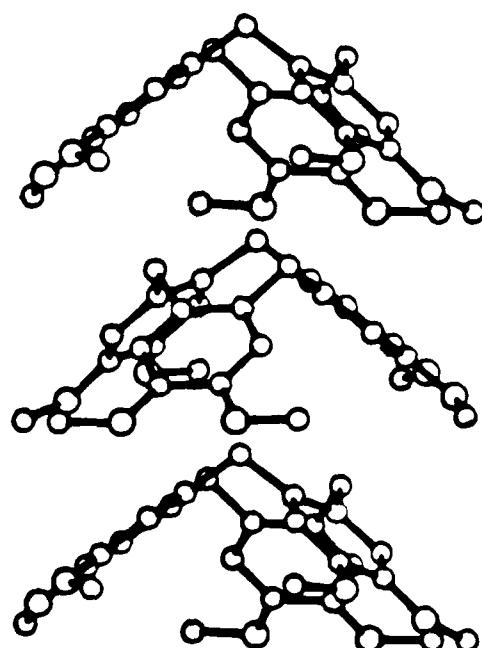
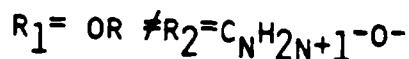
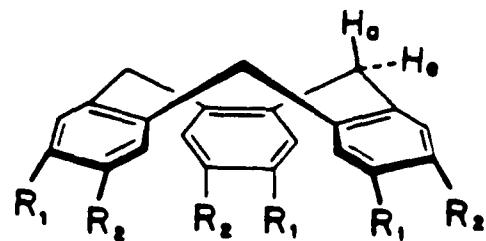
The first disc-like liquid crystals were reported only in 1977 (28). Scheme 13 presents the types of mesomorphic phases exhibited by disc-like derivatives. The first examples of main chain and side-chain LCP containing disc-like mesogens were synthesized by Ringsdorf's group (29, 30). At the first site the complicated structures outlined in Scheme 13 do not have



Scheme 13. A schematic representation of the molecular arrangement (a) in the nematic phase N_D ; (b) in the cholesteric phase N^* ; (c) in a columnar phase D, of disc-like liquid crystals



Scheme 14. Synthesis of hexasubstituted triphenylenes

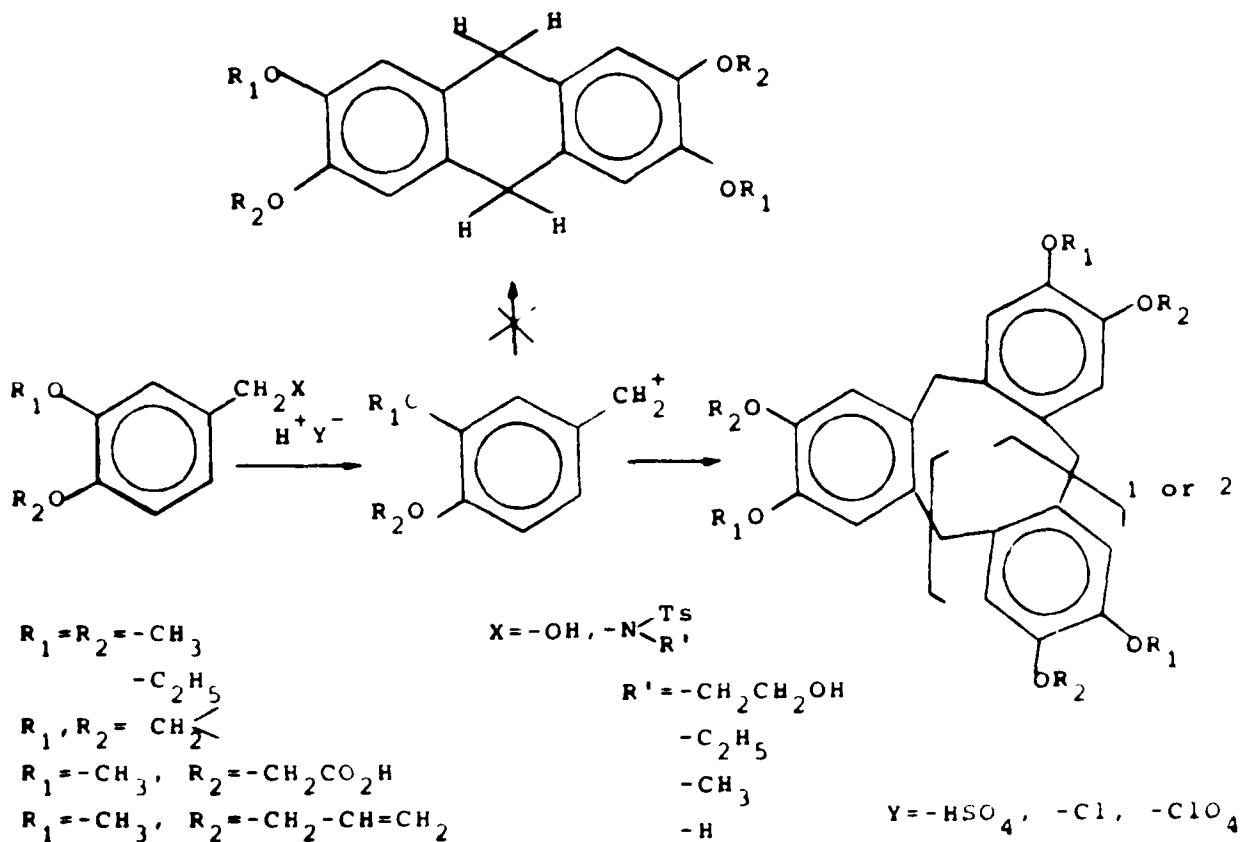


Scheme 15. Detail of the columnar stacking of cyclo-triveratrilene molecules in the crystal state

much to do with cationic reactions. Nevertheless, two of the most frequently employed disc-like molecules are prepared by cationic oligomerization.

Scheme 14 presents the cyclotrimerization of 1,2-dialkoxybenzenes to form hexaalkoxytriphenylenes. Initially this reaction was performed by chemical oxidation of 1,2-dimethoxybenzene (i.e., veratrole) (31, 32) and later of the 1,2-dialkoxybenzenes (33) with chloranil in sulfuric acid. Later, it has been shown that this unexpectedly free of side reaction cyclotrimerization can be performed by anodic oxidation of the 1,2-dialkoxybenzenes in a nonnucleophilic solvent like a mixture of dichloromethane and trifluoroacetic acid, while ESR spectroscopy has definitely demonstrated the cation-radical mechanism of this reaction (34, 35). This simple and quantitative cyclotrimerization has been recently applied to the synthesis of a novel class of polymers obtained through the cyclotrimerization of dibenzo-crown ethers (36, 37).

An other cyclotrimer synthesized by carbocationic cyclotrimerization is the cyclotriveratrilen-crown presented in Scheme 15. This crown molecule is of particular interest for the synthesis of host-guest systems (38, 39) and recently, the first cyclotriveratrilene derivatives exhibiting columnar or pyramidal mesophases became available (40 - 42). The synthesis of cyclotriveratrilene was reviewed elsewhere (39) and Scheme 16 summarizes only few examples of cyclotrimerization of the veratryl carbocation which was generated from several unusual functional groups, of particular interest being the veratrilamine N-tosylates.



Scheme 16. Synthesis of cyclotri(tetra)veratrilene

Although it has been considered for quite a while that the cyclooveratril carbocation generates 2,3,6,7-tetramethoxy-9,10-dihydroanthracene, apparently since this reaction is thermodynamically controlled, mostly the 10,15-dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononene) (i.e., cyclotriveratrilene), and in some cases also traces of cyclotetraveratrilene are obtained. As Scheme 16 shows, this cationic cyclotrimerization can tolerate a large variety of functional groups and this seems to be the consequence of the cyclooveratril cation stability. This apparently simple and little explored chemistry can certainly open new preparative avenues which were previously unexplored.

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